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54 Supported catalyst for the synthesis of 1-2 dichloroethane by oxychlorination of ethylene within a fluidized bed.

57 A supported catalyst for the C_2H_4 oxychlorination within a fluidized bed, comprising a Cu compound in amounts corresponding to a content from 1 to 10% by weight —as Cu metal— on a carrier preferably selected from the group consisting of microspheroidal Al_2O_3 , microspheroidal SiO_2 and microspheroidal silica-alumina, characterized in that the molar ratio (outer Me/outer Cu), as determined by means of XPS analysis, is at least 40% higher than the molar ratio:

$$\gamma = \frac{\text{total Me present within the catalyst}}{\text{total Cu present within the catalyst}}$$

wherein Me is e.g. Al, Si or Al + Si.

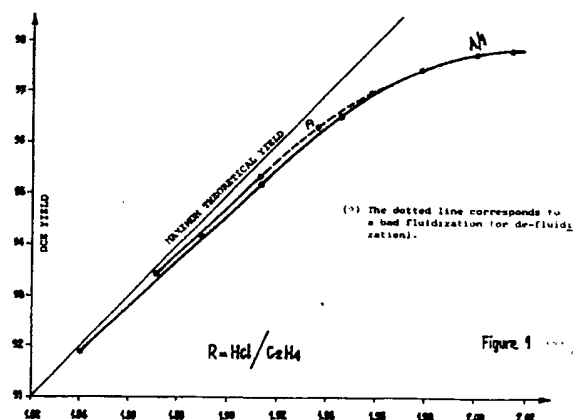


Figure 1

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SUPPORTED CATALYST FOR THE SYNTHESIS OF 1-2,DICHLOROETHANE
BY OXYCHLORINATION OF ETHYLENE WITHIN A FLUIDIZED BED

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The invention concerns a supported catalyst for the synthesis of 1-2,dichloroethane, hereinafter called DCE, obtained through ethylene
15 oxychlorination, said catalyst being used in the form of a fluidized bed.

The catalytic gaseous phase oxychlorination of C_2H_4 with HCl and O_2 (or gases containing same) is well known and was widely used for the
20 preparation of DCE, from which, in a subsequent stage (by pyrolysis), vinyl chloride is obtained.

Likewise it is known to use the catalytic mass in the form of a fluidized bed, in order to get rid of the considerable heat released by
25 both the oxychlorination reaction and the combustion of ethylene to CO and CO_2 ; the fluidized bed processes which realize conditions of almost a perfect isothermicity are those which up to now have achieved the best
30 results.

Catalytic compositions promoting the oxychlorination have already been described. The most common one is based on copper compounds, in general chlorides, supported in different amounts on microspheroidal
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supports (in general Al_2O_3) suitable, due to their granulometric distribution and resistance to friction wear, for use in fluidized beds. The previously described compositions present, however, many drawbacks which limit, and in certain instances hinder, satisfactory exploitation on an industrial scale. Thus, for instance, there are catalytic formulations characterized by high DCE yields with respect to HCl, which must work, however, with a high C_2H_4 excess, with respect to HCl, in order to prevent the phenomena of bad fluidization (even defluidization), whereby the DCE yields, with respect to ethylene, are rather unsatisfactory. The C_2H_4 excess, with respect to DCE, cannot, in fact, be converted into DCE and is therefore eliminated with the gaseous exhausts as unreacted C_2H_4 or in the form of carbon oxides (CO and CO_2).

On the other hand there are compositions which can work with a lower excess of C_2H_4 , with respect to HCl, without incurring particular problems of bad fluidization of the catalytic bed, thus operating with high DCE yields with respect to C_2H_4 , but which, on the contrary, lead to low HCl conversions. In the latter case it is necessary to use special equipment, withstanding HCl, in order to avoid corrosion. Furthermore it is necessary to neutralize the unconverted HCl with alkali, with a consequential increase in technical requirements. Moreover, certain compositions are characterized by the use of carriers different from Al_2O_3 , for instance SiO_2 or silica alumina, or by the presence in the catalyst, together with CuCl_2 , of other compounds, in general chlorides, of alkali or alkaline-earth metals and of rare

earths.

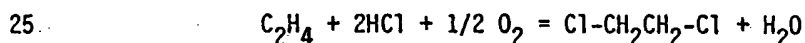
The following documents may be cited:

- Italian Patent 690,193, teaching the use of compositions based on CuCl_2 , alkaline-earth chlorides and rare earth chlorides, in order to reduce the extent of the combustion on a fluidized bed;
- British Patent 971,996, which exemplifies catalytic compositions based on CuCl_2 and alkaline-earth chlorides on either a fixed or fluidized bed.

None of these compositions overcomes completely all the drawbacks, with respect to a satisfactory industrial exploitation, namely:

- insufficient DCE yield, with respect to C_2H_4 ;
- insufficient conversion of HCl ;
- poor fluidization (even defluidization).

In order to better appreciate the importance of these drawbacks and, consequently, the importance of overcoming them, it may be useful to provide further specific information as to the bad fluidization phenomena, typical of the catalysts described herein-above. The reaction may be represented as follows:



what means that in order to obtain a 100% DCE yield, with respect to C_2H_4 , a mixture of HCl and C_2H_4 in a molar ratio of at least 2 must be fed besides oxygen. Thus, for instance, if HCl and C_2H_4 , in a 1.86 molar ratio, is fed into the reactor, the maximum theoretical DCE yield, with respect to C_2H_4 is: $1.86 : 2 \times 100 = 93$.

The yields that can be obtained are usually below this value, because of

incomplete conversion of HCl; in fact, if:

$R = \text{HCl}/\text{C}_2\text{H}_4$ molar feed ratio;

$C = \% \text{ of conversion of HCl} = \left(1 - \frac{\text{HCl moles at outlet}}{\text{HCl moles at inlet}}\right) \times 100,$

5 are used, it can be shown that the DCE yield, with respect to ethylene, is expressed by the equation: $\text{DCE yield} = (R/2) \times C$, so that, in order to obtain high yields, R and C must be both as high as possible. Within a
10 fluidized bed reactor, consisting of a catalyst based on CuCl_2 , supported on microspheroidal Al_2O_3 , prepared according to known technologies, the following phenomena occur:

- 15 - with relatively low $\text{HCl}/\text{C}_2\text{H}_4$ feed ratios, (e.g. lower than 1.9 moles) the fluidization is good, but, for the reasons stated herein-above, the DCE yield, with respect to ethylene, is limited (e.g. below 95%).
- 20 - increasing the $\text{HCl}/\text{C}_2\text{H}_4$ ratio, above the previously indicated values, worsens the fluidization and decreases the HCl conversion. This worsening can be perceived visually in pilot glass reactors and reveals itself by the formation of an increasing number of gas
25 bubbles of increasing diameter. When the diameter of the bubbles equals roughly the diameter of the reactor, the "rupture" of the catalytic bed can occur, i.e. inside the bed the formation of "empty" zones, alternated by "full" zones, can be seen. Under
30 extreme conditions, the catalyst is dragged out of the reactor.

In industrial reactors the worsening reveals itself in a less striking but still evident way through the undue loss of catalyst in the

cyclones, due to the clogging of the cyclones' legs, which hinders the flowing back, into the catalyst bed, of the catalyst separated at the head of the cyclones. In both cases it is impossible to carry out normal
5 operations and it is necessary to decrease the $\text{HCl}/\text{C}_2\text{H}_4$ feed ratio until a good fluidization is restored or, in extreme cases, to switch off the feed of the reactants.

The causes of these phenomena have been generically ascribed to
10 the so called "stickiness", that hinders the free moving or reciprocal creep of the single granules, within the catalytic bed, because of the formation of clots that are difficult to fluidize (whereby the bubbles) and slightly flowable (whereby the clogging of cyclones' legs).
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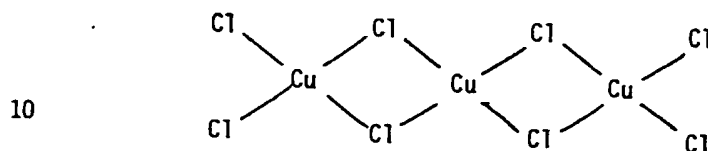
The sticking can be observed only in connection with the increase of the $\text{HCl}/\text{C}_2\text{H}_4$ feed ratio and is reversible. These indications mean that the active part of the catalyst namely Cu is responsible for said
20 phenomena (rather than the carrier, whose features do not substantially depend on said ratio). In fact, if the results of many kinetic works are analysed, it is possible to trace nearly always a mechanism involving:

- 1.- the reaction of C_2H_4 with Cu_2Cl_4 , in order to give DCE and Cu_2Cl_2 ;
- 25 2.- the oxidation of CuCl_2 with O_2 (air), to give Cu_2OCl_2 and H_2O ;
- 3.- the reaction of 2HCl with Cu_2OCl_2 to give again Cu_2Cl_4 and H_2O .

In other words Cu shifts cyclically from Cu_2Cl_4 (chlorided Cu) to Cu_2Cl_2 (reduced Cu) to Cu_2OCl_2 (oxychlorided Cu) and at last again to
30 Cu_2Cl_4 . The equilibrium between such forms depends essentially on the $\text{HCl}/\text{C}_2\text{H}_4$ feed ratio; when the ratio increases the chlorided form becomes prevailing, while at low values of said ratio the oxychlorided form is

prevailing.

The occurrence of sticking may thus be explained by a predominance of Cu_2Cl_4 on increase of the $\text{HCl}/\text{C}_2\text{H}_4$ ratio. On the other hand, there is evidence of the trend of Cu_2Cl_4 to form polymers (Kenney C.N., Catal. Rev. Sci. Eng. 11 (2), 197 (1975)):



One solution to the problems is suggested by Italian Patent Publication 25,941 A/81, wherein the Applicant describes a method for the preparation of a catalyst free from the drawbacks typical of the catalysts previously described. Said method comprises the impregnation of a performed catalyst, consisting of CuCl_2 supported on Al_2O_3 , by means of an aqueous solution of MgCl_2 , whereupon the catalyst is dried and activated in air at temperatures up to 300°C . Despite the excellent performance of this catalyst, it is useful to manufacture catalysts possessing even better properties.

One object of the present invention is that of providing in the most simple and effective way, a catalyst for the C_2H_4 oxychlorination to DCE, suitable for use in fluidized beds, displaying best the properties required in view of a satisfactory industrial exploitation, namely:

- 30
- a high DCE yield, with respect to C_2H_4 ;
 - a high conversion of HCl ;
 - excellent fluidization properties.

The invention concerns a supported catalyst for the synthesis of 1,2-dichloroethane (by means of C_2H_4 oxychlorination within a fluidized bed) comprising a Cu compound in amounts corresponding to a content from 1 to 10% by weight -as Cu metal- on a carrier preferably selected from the group consisting of microspheroidal Al_2O_3 , microspheroidal SiO_2 and microspheroidal silica-alumina, characterized in that the molar ratio (outer Me/outer Cu), as determined by means of XPS analysis (as described within the examples, the XPS technique allows the analysis of a surface layer having a thickness from 2 to 3 nm (nanometers)) is at least 40% higher than the molar ratio:

$$Y = \frac{\text{total Me present within the catalyst}}{\text{total Cu present within the catalyst}}$$

wherein Me is Al, Si, Al + Si or whatever metal otherwise contained in the carrier.

Preferably the molar ratio (outer Me/outer Cu) is equal to or higher than 20:1 and the Cu concentration on the outer surface of the carrier is zero or any way much lower than the Cu concentration in the layers immediately underlying the analyzed surface layer. Interesting results were obtained with a ratio (outer Me/outer Cu) between 40:1 and 53:1. Said catalyst comprises advantageously also a Mg compound, the Mg amounts being usually from 0.2 to 0.8 moles of Mg per mole of Cu.

In order to obtain a catalyst characterized by low Cu concentration on the outer surface of the granules and having, as such, the features required by a satisfactory industrial exploitation, different ways may be used and particularly the following two methods.

I) The first method is characterized in that a preformed catalyst of the usual type, based on CuCl_2 supported e.g. on Al_2O_3 , is impregnated in its dry state with an aqueous solution (of a volume substantially equal to the volume of the pores of the carrier), containing a strong acid, for instance HCl , in amounts corresponding to at least 1 equivalent per mole of Cu (present in the catalyst) and preferably also containing MgCl_2 in amounts from 0 to 1 mole per mole of Cu (present in the catalyst), the catalyst being preferably dried (e.g. at 110°C) after impregnation, and subsequently activated in air (e.g. for 4 hours between 180°C and 300°C). In this way it is possible to obtain a catalyst from the outer surface of which the major portion of Cu (present in the starting pre-formed catalyst) was removed.

II) The second method is characterized in that a carrier is impregnated in the dry state with an aqueous solution (of a volume substantially equal to the volume of the pores of the carrier) containing a Cu compound, in such an amount as to load into the final catalyst, a Cu amount, expressed as metal, from 1 to 10% by weight, and containing, moreover, an acid and a Mg compound, in amounts equal to at least 1 equivalent of acid and from 0 to 1 mole of Mg per mole of Cu , the catalyst being preferably dried, after impregnation, and then being activated in air between 180° and 300°C .

Also in this case it is possible to obtain a catalyst on whose outer surface the Cu content is kept at a minimum. The Mg compound corresponds preferably to the Cu compound in the sense that, for instance, in the case where salts are used, the Mg is derived from the

same acid as the Cu salt. Analogously said salt must correspond to the Cu compound. If the Cu compound is CuCl_2 , the acid will thus be HCl while the Mg compound will be MgCl_2 .

5 The catalyst according to the invention is characterized by a minimum or zero (and at any rate definitely lower than that of the catalysts already described) concentration of Cu on the outer surface of the granule, as shown by results from the determinations carried out
10 with the technique known as X-Ray Photoemission Spectroscopy (henceforth XPS), and, as such, displays excellent fluidization properties and maintains high HCl conversions, even in the case of high $\text{HCl}/\text{C}_2\text{H}_4$ ratios so that it is possible to reach high DCE yields with respect to C_2H_4 .
15 The inner Cu, although acting in the conversion cycles and in the equilibria between the various forms (CuCl_2 , Cu_2Cl_4 , etc.), depending on the $\text{HCl}/\text{C}_2\text{H}_4$ feed ratio, does not give rise to the sticking phenomena
20 which, on the contrary, involve zones of possible contact between the different granules.

The main feature of the catalyst according to the invention, is that the active part is almost completely segregated inside the pores of
25 the carrier, whereby the Cu concentration on the outer surface is at a minimum, and any way lower than that of conventional catalysts, as shown by XPS measures, and at said minimum the concentration also remains after long periods of time.

30 The use of this catalyst allows the reaction to be performed within a fluidized bed, using, without any bad fluidization, high $\text{HCl}/\text{C}_2\text{H}_4$ ratios in the feed and (particularly when the catalyst contains

Mg) high conversions of HCl and high DCE yields (with respect to C_2H_4) are thus obtained, in accordance with the equation: yield of DCE = $RxC/2$.

5 The operative oxychlorination conditions do not substantially differ from those typical for the catalysts previously described.

C_2H_4 , HCl and gases containing O_2 (in general air), fed in gaseous phase, are then pre-heated to a temperature from 200 to 250°C,
10 preferably from 220° to 235°C.

 The other operative parameters, in general, are comprised between the following ranges:

15 A) Air/ C_2H_4 ratio: such that the O_2 content, in the gaseous exhausts, after condensation of DCE, H_2O and HCl, is from 3 to 10% by volume.

20 B) HCl/ C_2H_4 ratio: the nearest possible to the stoichiometric value (2/1 molar), compatible with good fluidization conditions of the catalytic bed and of a sufficiently high conversion of HCl, conditions which depend on the type of catalyst.

25 C) Contact time (expressed as a ratio between the volume of the catalytic bed in a fluidized state, and the volumetric flow rate of the mixture of reactants, at the temperature and pressure conditions existing in the catalytic bed): it depends essentially on the type of the catalyst used; in general it is from 10 to 40,
30 preferably from 20 to 30 seconds.

D) Linear velocity of the gases: within the range between the minimum fluidization rate and the dragging speed, both being typical for

each type of catalyst; in general said velocity is from 10 to 50, preferably from 20 to 40 cm/s.

- 5 E) Total pressure during the reaction (relevant for achieving an effective contact between the reactants, in a gaseous phase, and the catalyst, in a solid phase): in general pressures greater than atmospheric pressure and up to 600 kPa are used; at greater pressures, energy waste becomes predominant, due to the compression work.
- 10

The following examples are given for purely non-limitative illustrative purposes.

OPERATIVE CONDITIONS COMMON TO DIFFERENT EXAMPLES

- 15 The catalysts cited in the examples (except preformed catalyst 'A') were prepared by impregnation in the dry state with an aqueous solution, dried at 110°C and activated in air for 4 hours at the temperature (either 180° or 300°C) indicated on Table 1, which also reports the results of the XPS analysis. The measurements of the outer surface concentration of Cu were carried out following the XPS technique (cf. C.D. Wagner: "Handbook of X-ray Photoemission Spectroscopy; Perkin Elmer Co., Eden Prairie; 1979), based on X-ray irradiation and on measuring the energy level and the energy intensity of the electrons emitted by the solid. The energy level of said electrons is characteristic for the element while the energy intensity is proportional to the number of atoms present in the volume of sample, to a depth substantially from 2 to 3 nm (20 - 30 Å) from the surface. As the mean granulometric size of the catalyst is around 50 µm (micrometers)
- 20
- 25
- 30

and usually ranges from 20 to 80 μm are cited, the measures of the atomic concentrations refer to about 1 tenthousandth of the diameter of the granule, namely, essentially, to its outer surface. A small amount of sample (just a few mg) was pressed onto a pure indium plate in order to obtain an analyzable surface of an area equivalent to a few sq. mm . The samples were then analyzed under a high-pushed vacuum, at a basic pressure of $2 \times 10^{-7} \text{ Pa}$, using an X-ray source operating at 400 W and fitted with a Mg-anode (K alpha radiation of magnesium). The photo-emission spectra of the present elements, that is O/1s, C/1s, Cl/2p, Mg/2p, Al/2p, were then gathered together under conditions of high resolution by using a computer suitable for the digitalized acquisition of the data, with a maximization of the signal noise ratio. After removal of the background noise, the areas of the photoemission peaks were calculated by means of numerical integration. The intensity value thus obtained, corrected for the respective sensitivity factor, was directly proportional to the surface atomical concentration of the respective element.

EXAMPLES from 1 to 6 (preparation of the catalyst)

Catalyst 'A' is a usual (commercially available) preformed comparison catalyst, based on CuCl_2 , supported on a microspheroidal alumina carrier, having a Cu content (as a metal) of 5% by weight, while comparison catalyst 'B' was prepared by impregnation in the dry state of a carrier (consisting of microspheroidal alumina with a mean particle diameter of 50 μm) with an aqueous solution (with a volume equal to the volume of the pores of the carrier) containing CuCl_2 , thereby obtaining

a catalyst with a final Cu content (expressed as a metal) of 5% by weight. The outer coating degree can be better represented by the Al/Cu ratio which, independently from possible variations in the corresponding amounts of oxygen and chlorine, gives the "frequency" of Cu atoms with respect to Al atoms. In this way the outer surface of catalysts A and B is characterized by the presence of one Cu atom every 10 Al atoms, as indicated on Table 1.

10 Catalyst 'A/1' was prepared by impregnating in the dry state catalyst 'A' with an aqueous solution (of a volume equal to the volume of the pores of the catalyst), and containing 2 moles of HCl and 0,75 mole of $MgCl_2$ per moles of Cu (contained in the catalyst). According to
15 Table 1, the outer surface Cu is reduced fourfold (4 times) with respect to catalyst A.

Catalyst 'B/1' was prepared by impregnating in the dry state the
20 carrier used for preparing catalyst B with an aqueous solution (of a volume equal to the volume of the pores of the carrier). Said solution contained:

- $CuCl_2$ in such an amount to obtain 5% by weight of Cu on the
25 global weight of the catalyst;
- 2 moles of HCl per mole of Cu;
- 0,75 moles of $MgCl_2$ per mole of Cu.

According to Table 1, catalyst B/1 have an outer surface Cu
30 concentration reduced four to fivefold with respect to catalyst B. Let us now summarize hereinbelow the most significant ratios.

15

20

25

30

TABLE 2

Ex. n°	Catalyst	$\frac{Al}{Cu}$	Activation temperature T (°C)	Oxychlorination T (°C)	HCl/C ₂ H ₄ (by moles)	DCE yield (molar % on fed C ₂ H ₄)	HCl conversion (%)	Fluidization
7	A	10	-	220	1.871	93.45	99.89	good
8	A	10	-	220	1.913	95.35	99.69	good
9	A	10	-	220	1.936	96.35	99.53	bad
10	A	10	-	220	1.958	97.00	99.08	defluidizes
11	A/1	40	180	225	1.844	91.90	99.89	excellent
12	A/1	40	180	225	1.936	96.25	99.40	excellent
13	A/1	40	180	225	2.014	97.80	97.12	good
14	A/1	40	300	225	1.889	94.20	99.70	excellent
15	A/1	40	300	225	1.945	96.55	99.28	excellent
16	A/1	40	300	225	2.016	97.70	96.93	good
17	B	10	180	220	1.920	95.47	99.54	good
18	B	10	180	220	1.980	97.05	98.10	bad
19	B	10	180	220	2.029	-	-	defluidizes
20	B/1	45	180	225	1.840	91.90	99.83	excellent
21	B/1	45	180	225	1.889	94.20	99.75	excellent
22	B/1	45	180	225	1.945	96.59	99.30	excellent
23	B/1	45	180	225	2.016	97.68	96.90	good
24	B/1	53	300	225	1.936	96.24	99.40	excellent
25	B/1	53	300	225	2.014	97.86	97.20	good
26	B/1	53	300	225	2.089	97.93	93.80	good

EXAMPLES from 7 to 26 (behaviour of the catalyst)

Into a glass reactor having a diameter of 4 cm and a height of 3 m., suitable for withstanding pressures up to 600 kPa, were introduced the prepared catalysts and then they were tested in the form of a fluidized bed (in the oxychlorination of C₂H₄) under the following conditions:

. P = 4 absolute atm.;

- . contact time: 28 sec.;
- . $\text{air/C}_2\text{H}_4 = 3.2$ (by moles).

The values of oxychlorination temperature and of the ratio
5 $R = \text{HCl/C}_2\text{H}_4$, are reported on Table 2, along with the results.

Examples 7 to 16 show that, corresponding to the lower concen-
trations of outer surface Cu, the better fluidization properties of
catalysts A/1 allow to operate at higher $\text{HCl/C}_2\text{H}_4$ ratios, so as to
10 provide better DCE yields with respect to catalyst A. The comparison
becomes even more evident from the graph in figure 1. The same may be
said for examples from 17 to 26 and therefore for the excellence of
catalysts B/1 with respect to catalyst B (see fig. 2).
15

CLAIMS

1.- A supported catalyst for the synthesis of 1,2-dichloroethane
(by means of C_2H_4 oxychlorination within a fluidized bed) comprising a
5 Cu compound in amounts corresponding to a content from 1 to 10% by
weight -as Cu metal- on a carrier preferably selected from the group
consisting of microspheroidal Al_2O_3 , microspheroidal SiO_2 and
microspheroidal silica-alumina, characterized in that the molar ratio
10 (outer Me/outer Cu), as determined by means of XPS analysis (as
described in the examples), is at least 40% higher than the molar ratio:
total Me present within the catalyst

15
$$Y = \frac{\text{total Me present within the catalyst}}{\text{total Cu present within the catalyst}}$$

wherein Me is Al, Si, Al+Si or whatever metal otherwise contained in the
carrier.

2.- A catalyst according to claim 1, wherein said Cu content is
20 from 3 to 8% by weight.

3.- A catalyst according to claim 1, wherein the molar ratio
(outer Me/outer Cu) is equal to or higher than 20:1.

4.- A catalyst according to claim 1, wherein the Cu concentration
25 on the outer surface of the carrier is zero or any way much lower than
the Cu concentration in the layers immediately underlying the analyzed
surface layer.

5.- A catalyst according to claim 1, wherein said catalyst also
30 comprises a Mg compound, the Mg amount being from 0 to 1 and
particularly from 0.2 to 0.8 moles per mole of Cu.

6.- A method for the preparation of a catalyst according to claims 1 to 5, characterized in that a preformed catalyst of the conventional type, based on CuCl_2 supported on Al_2O_3 , SiO_2 or silica-alumina, is
5 impregnated in the dry state with an aqueous solution (of a volume substantially equal to the volume of the carrier's pores) containing a strong acid, e.g. HCl , in amounts corresponding to at least 1 equivalent per mole of Cu (present in the catalyst), said acid solution also
10 preferably containing a Mg compound in amounts from 0 to 1 moles of Mg per mole of Cu (present in the catalyst).

7.- A method for the preparation of a catalyst according to claims 1 to 5, characterized in that a carrier is impregnated in the dry state
15 with an aqueous solution (of a volume substantially equal to the volume of the carrier's pores) containing a Cu compound in such amounts so as to produce, in the final catalyst, a Cu content (expressed as a metal)
20 from 1 to 10% by weight, and containing, moreover, an acid and a Mg compound, in amounts equal to at least 1 equivalent of acid and between 0 and 1 mole of Mg per moles of Cu respectively.

8.- A method according to claim 7, wherein said Mg compound
25 corresponds to the Cu compound in the sense that, in the case where salts are used, the Mg salt is derived from the same acid as the Cu salt.

9.- A method according to claim 1, wherein said acid corresponds
30 to the Cu compound.

10.- A method according to claim 8 or 9, wherein the Cu compound is CuCl_2 , the acid is HCl and the Mg compound is MgCl_2 .

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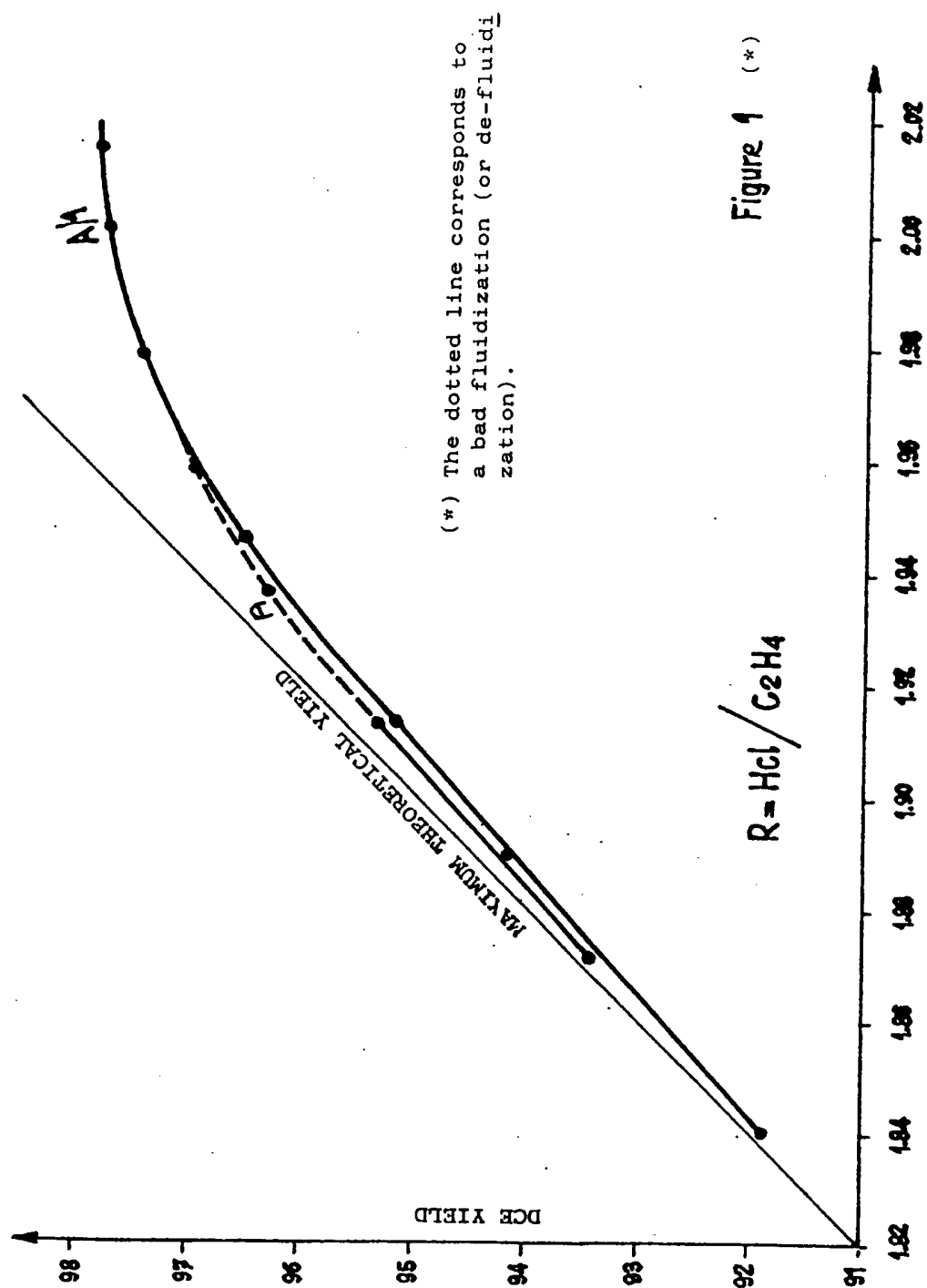


Figure 1 (*)

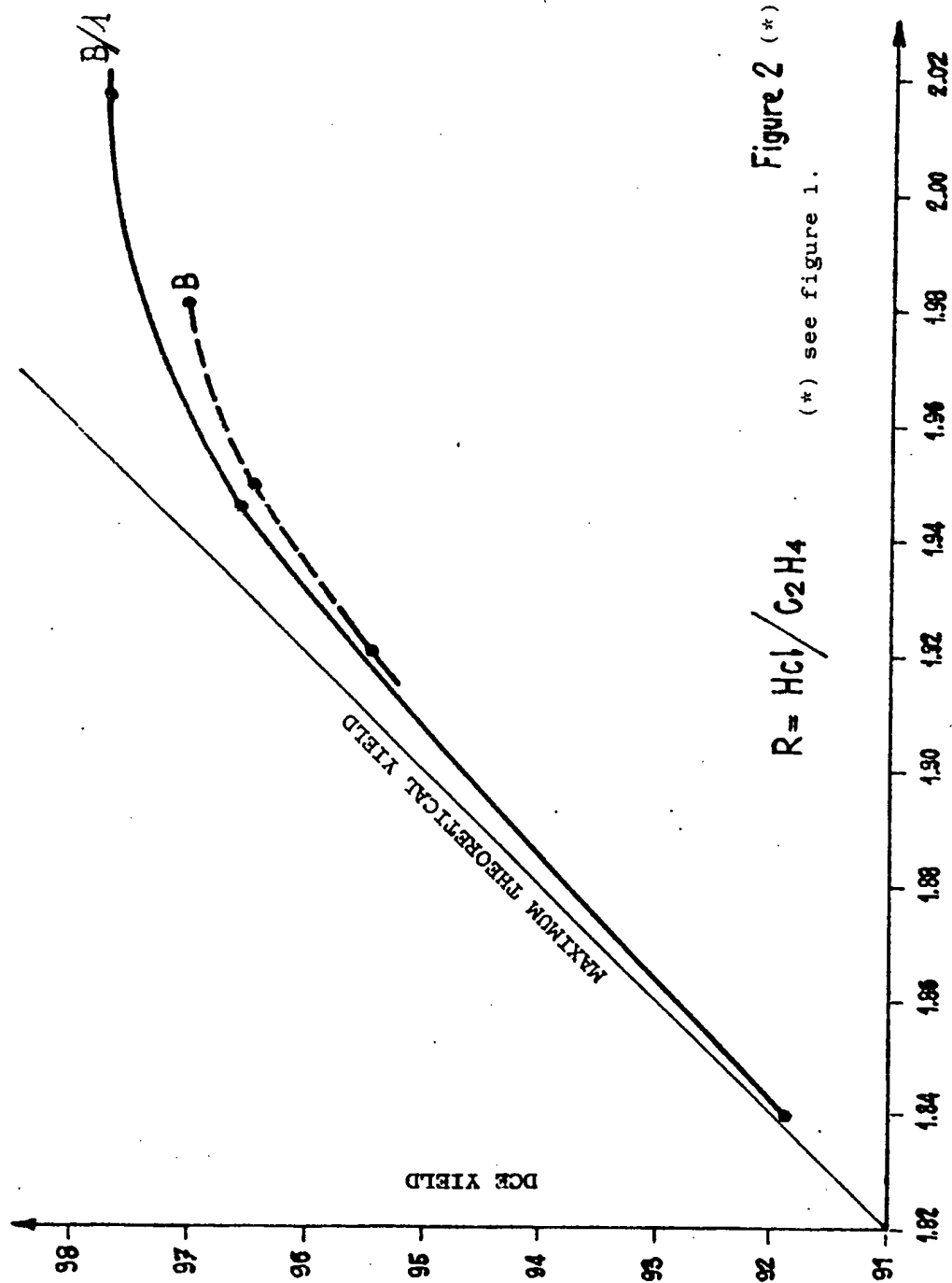


Figure 2 (*)

(*) see figure 1.